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CONTRIBUTIONS FROM THE CHEMICAL LABORATORY OF HARVARD COLLEGE.

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Presented by T. W. Richards. Received September 2, 1905.

As the result of certain speculations concerning metallic conductivity and the possibility of a gradual transition * from metallic to electrolytic conductivity, one of the authors was led several years ago to investigate the conductivity of liquid iodine † and of solutions in that solvent. The results of the preliminary experiments, although promising no definite answer to the questions which originally suggested the experiments, were considered of sufficient interest to warrant the present more extended research.

In the last decade our knowledge of conductivity in non-aqueous solutions has grown rapidly, and many new solvents, chiefly oxygen and nitrogen compounds, have been found to give conducting solutions. All of the inorganic solvents which have been studied, if we except sulphur dioxide and certain less important compounds of sulphur and of phosphorus, are salts or substances of similar dualistic type.

At the time when our work was begun no element had been found to act as a dissociating agent, but recently a paper by Plotnikow ‡ on

* Cf. Quincke, Zeit. anorg. Chem., **24**, 220 (1900).

† It may seem to the chemist a little odd to regard iodine as in any way allied to the metals, but in the periodic classification it stands among the elements which are on the border line between the metals and the non-metals, and which frequently partake of the character of both; thus if we consider the elements of the three adjoining groups, P, As, Sb; S, Se, Te; Cl, Br, I, we observe that in the first group arsenic and antimony both have marked metallic characteristics, in the second group tellurium is usually regarded as a metal, while one of the modifications of selenium is metallic, and so we might expect that in the last group iodine would show some metallic properties. It does in fact possess metallic lustre, that is, it behaves like a metal towards electric waves of high frequency.

‡ Zeit. phys. Chem., **48**, 220 (1904).

conductivity in bromine solutions has appeared. The extraordinarily interesting and puzzling phenomena that he has studied appear to have little in common with those we are about to discuss, notwithstanding the close relationship between bromine and iodine.

Iodine bears no resemblance to any of the other dissociating solvents, except bromine, which have been studied. One property, however, it possesses in common with them all, the tendency to form complexes.* Thus Walden and Centnerszwer have shown liquid sulphur dioxide to be an excellent dissociating agent,† and have also pointed out the large number of complexes into which this substance enters.‡ Ammonia, which forms such a bewildering number of complex compounds, has been shown by Franklin and Kraus § to be one of the very best dissociating solvents. The case of water is too familiar to dwell upon.

The complexes in which iodine occurs have, with the exception of the polyiodides, been little studied, but doubtless a very large number could be isolated. Almost all salts increase the solubility of iodine in water, indicating the formation of complexes. The various solvents too, in which iodine dissolves with a brown color, are known to enter into combination with it.‖

The dielectric constant of iodine has not been determined, as far as we know.

In undertaking the investigation of iodine solutions we had the option of making a cursory study of a large number of substances or a more thorough study of some one substance. Choosing the latter course we have determined with a fair degree of accuracy the conductivity of solutions of potassium iodide in liquid iodine at temperatures from 120 degrees to 160 degrees, and in concentrations ranging from a few thousandths normal up to 10 times normal, — a range in which the specific conductivity increases 10,000 times.

Experimental Method.

The conductivity cells were of the form shown in Figure 1. They were made of two tubes 1½ cm. in diameter and 15 cm. long, joined below by a smaller tube 8 or 10 cm. long and 3 mm. in diameter. The ends of the cell were closed by tight-fitting glass stoppers. The elec-

* See Abegg, Zeit. elek. Chem., **5**, 353 (1899).
† Zeit. phys. Chem., **39**, 513 (1901).
‡ Zeit. phys. Chem., **42**, 432 (1903).
§ Amer. Chem. Jour., **23**, 277 (1900).
‖ Strömholm, Zeit. phys. Chem., **44**, 721 (1903).

trodes (4 sq. cm.) of polished platinum foil were, in the early experiments, attached to platinum wires leading through the sides of the tubes. Later, in order to prevent any possible conduction through the thermostat liquid, these wires were carried down inside the tubes from the top and fastened rigidly below by small rods of glass. This arrangement was fairly satisfactory for dilute solutions, which attack platinum only slightly and superficially, but with solutions stronger in potassium iodide the platinum suffered seriously, the electrode being sometimes nearly eaten away in the course of a few days. For this reason it was desirable to use electrodes which could be removed except during measurements. Electrodes attached to the stoppers, as shown in the figure, proved to be satisfactory in every respect and were used in all the later experiments. Between measurements these stoppers with their electrodes were replaced by plain glass stoppers of similar form. On account of the density of iodine vapor it was found that this could be done without appreciable loss of iodine. The small changes of position in the electrodes that were possible were shown to have no noticeable effect on the resistance of the cell. These movable electrodes had the further advantage that they could be cleaned before each measurement.

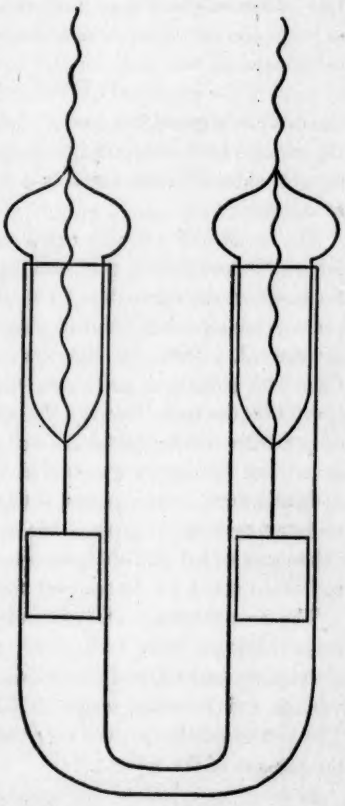

FIGURE 1.

Even with this arrangement, since it was sometimes necessary to leave the electrodes in the solution for an hour or two, it was feared that the platinum might be sufficiently attacked to influence the results. For this reason we used for all concentrated solutions electrodes of platinum-iridium foil and wire, containing 15 per cent iridium. These when first

used were slightly etched on the surface, but afterwards they appeared to be unattacked even after long standing in concentrated solutions.

The cells were immersed nearly to the top in the thermostat, which was of the ordinary type and so arranged that it could be readily set at any one of three temperatures, 120°, 140°, and 160°. At first cotton-seed oil was used for the bath, but was later discarded, partly on account of the vapors which, rising from it and condensing on the sides of the cell, endangered the purity of the contents, and partly on account of the gradual hardening which it underwent. After some experimenting a suitable substance was found in a commercial substitute for lard known as cottolene.

The method of carrying out a series of experiments was as follows: Enough iodine (60–80 gm.) was weighed out to stand when melted 2 or 3 cm. above the electrodes. The glass stoppers were inserted at once to prevent loss of iodine, the cell placed in the thermostat, and its resistance determined. Then the stoppers were removed, after gently warming them with a flame to melt down the small quantity of iodine which sublimed into the space between the stopper and the tube. A known weight of potassium iodide, pulverized and pressed into a small pellet, was introduced, and the liquid was stirred by a simple apparatus which drew it back and forth from one arm of the cell to the other. The stoppers were replaced and the resistance again determined. In the same way more iodide was added and the process repeated. At each concentration the resistance could be determined for a number of temperatures.

The measurements of resistance were made by means of a Wheatstone's bridge, both with direct current and galvanometer, and with alternating current and telephone. The direct current was very convenient and accurate, and with dilute solutions gave excellent results. The two electrodes showed no potential difference either before or during the passage of the current. *

In order to calculate the specific resistance of the solution from the observed resistance, the constant of each cell was obtained by means of a standard aqueous solution of potassium chloride or potassium iodide.

The only chemicals used in the research were potassium iodide and iodine. The former was purified by several recrystallizations. Two kinds of iodine were used; one was the pure resublimed iodine prepared

* This lack of polarization is no evidence that the conductivity is metallic in character. The same phenomenon is observed with an aqueous solution of potassium iodide and iodine.

by Kahlbaum, the other was made according to the method of Andrews,* by heating together potassium bichromate and potassium iodide. Both varieties were further purified by resublimation and gave identical results. For determining the conductivity of pure iodine a still purer variety was desired. Its preparation will be described later.

Experimental Results.

In the first experiments measurements were made at the three temperatures, 120°, 140°, and 160°. Later, on account of certain irregularities at the lowest temperature, measurements were confined to the two higher at which uniformity in the composition of the solution could be established with less difficulty.

A large number of experiments made before the technical difficulties were entirely overcome need not be considered in detail, as they were followed by more accurate experiments covering the whole field. The example given in Table I (Preliminary Series) will suffice to show the general character of the results. L represents the specific conductivity. C expresses the strength of the solution in grams of potassium iodide to 100 grams of iodine. For the sake of convenience we will refer to this as the concentration. We have not yet made exact enough determinations of the specific gravities of the different solutions to enable us to give the true concentrations in gram-molecules per liter, but for dilute solutions this molecular concentration may be considered as proportional to C.

TABLE I.

Preliminary Series.

C.	L.		
	120°	140°	160°
0.	.0000644	.0000613	.0000563
.0315	.000228	.000214	.000195
.0561	.000402	.000362	.000336
.108	.000678	.000648	.000592
.162	.00110	.00102	.000932
.222	.00174	.00165	.00135

* Amer. Chem. Jour. **30**, 428 (1903).

We note at once the marked decrease of conductivity with increase of temperature. This negative temperature coefficient, although it suggests the behavior of metals, in no way proves that we are dealing here with a case of metallic conductivity. Many electrolytic conductors are known which show the same behavior; usually, it is true, in the case of solvents not far removed from their critical temperatures, but even in water a few substances, such as phosphoric acid, have negative coefficients. We shall see presently how the temperature coefficient of the iodine solutions changes with the concentration.

It is also evident from the table that the conductivity increases rapidly with the concentration and in fact more rapidly than the concentration itself. This fact can be better shown if we pass at once to the consideration of the following tables, containing Series 1 and 2. In these tables M represents the quotient $\frac{L}{C}$, and is therefore for these dilute solutions proportional to the molecular conductivity. Before taking this quotient we have subtracted from the observed values of L the specific conductivity of the iodine, thus correcting for the original conductivity of the solvent, as is customary in aqueous solutions.

TABLE II.

Series 1. 140°.

C.	L.	M.
0.	.0000216	
.0135	.0000970	.00555
.0246	.000141	.00484
.0471	.000240	.00464
.0688	.000340	.00464
.0901	.000455	.00480
.206	.00133	.00638
.325	.00271	.00828
.495	.00587	.0118
.671	.0107	.0159
.899	.0185	.0207
1.13	.0277	.0244

TABLE III.

SERIES 2.

C.	L.		M.	
	140°	160°	140°	160°
0.	.000068	.000066 (?)		
.00991	.000114	.000107	.0045	.0041
.0237	.000172	.000162	.00436	.00405
.0512	.000298	.000272	.00450	.00402
.0729	.000399	.000366	.00454	.00413
.0962	.000538	.000494	.00489	.00444
.123	.000706	.000656	.00518	.00479
.183	.00119	.00110	.00611	.00562
.236	.00178	.00163	.00725	.00662
.348	.00342	.00315	.00961	.00889
.461	.00541	.00515	.0116	.0110
.681	.0114	.0108	.0166	.0158
.900	.0194	.0185	.0213	.0204
1.12	.0275	.0269	.0243	.0239

The results contained in Series 2 are expressed graphically in Figure 2, the lower points representing the values at 160°, the upper those at 140°. It is evident that the values of M increase rapidly with the concentration. This phenomenon, although it has never been observed in aqueous solutions, is not rare in the case of other solvents. The figure shows further that between $C = 0.1$ and $C = 1.0$, M increases *linearly* with the concentration. The form of that portion of the curve lying below $C = 0.1$ deserves little attention, as the values here are much affected by the correction made for the original conductivity of the iodine, and are thus liable to large errors, even assuming that our method of making the correction is entirely correct in theory.

Above $C = 1.0$ the line shows the beginning of a curvature which becomes much more pronounced at slightly higher concentration.

The results obtained at 140° over a wide range of concentration are given in Series 3, 4, 5, 6, 7, and 8. All the values in these series, together with all but the first three points of Series 2 (140°) are plotted in Figure 3 and give a view of the values of M over a wide range of

TABLE IV.

C.	L.	M.	C.	L.	M.
Series 3.			Series 5.		
1.53	.0420	.0274	1.47	.0350	.0237
2.28	.0730	.0318	2.12	.0690	.0326
3.09	.113	.0367	2.77	.0980	.0356
3.64	.141	.0388	3.56	.140	.0394
4.45	.177	.0398	4.25	.174	.0410
13.2	.384	.0290	6.89	.273	.0398
Series 4.			8.99	.321	.0359
1.49	.0370	.0247	Series 6.		
2.03	.0625	.0307	1.34	.0368	.0274
2.56	.0895	.0350	20.1	.383	.0190
3.13	.119	.0380	Series 7.		
3.82	.153	.0400	23.2	.390	.0168
4.39	.179	.0409	Series 8.		
5.02	.233	.0415	28.1	.396	.0141
8.06	.312	.0390			
10.52	.355	.0338			
14.25	.394	.0276			

concentration. The points in the right hand portion of the curve, although few in number, were determined with more accuracy than any of the others. It is to be noted that for concentrations above 13, the specific conductivity is nearly constant.

The temperature coefficient of the conductivity, which in the case of

dilute solutions we have shown to be negative, becomes numerically smaller with increasing concentration, is zero when C is a little less than 3.0 and for stronger solutions becomes positive. The conductivity curve for any other neighboring temperature is therefore very similar to the one for 140°, but crosses that curve at a concentration of about 3. The change in sign of the temperature coefficient might perhaps have been predicted, for with increasing concentration the substance approaches more and more nearly the condition of a pure molten salt and all salts which have been hitherto studied have large positive temperature coefficients.

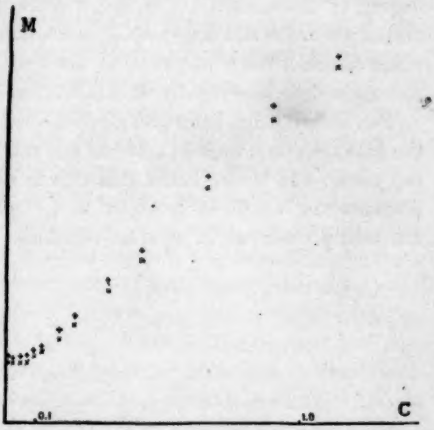

FIGURE 2.

Table V gives the percentage change in the conductivity, per degree, at several concentrations.

TABLE V.

C.	Temperature coefficient.
	per cent.
0.1	−0.46
0.4	−0.38
2.8	±0.
8.3	+0.30
20.0	+0.55
28.1	+0.67

DISCUSSION OF THE CONDUCTIVITY CURVE.

Assuming that the whole of the conductivity is electrolytic in character, let us consider from this point of view, the curves of Figures 2

and 3, especially the former, which embraces the region of dilute solutions. Here we may regard M as proportional to the molecular conductivity and, assuming the mobility of the ions to be constant, to the degree of dissociation. The latter quantity, instead of rising with increasing dilution and approaching a constant maximum as in the case of water solution, has a maximum in the neighborhood of $C = 5$, and from that point decreases rapidly with increasing dilution.

This behavior has been previously noticed by a number of observers in the case of certain organic solvents and other solvents of *small dissociating power*. It is our belief that this is an extreme manifestation of a phenomenon which is common to all solutions and which has been frequently observed in aqueous solutions.

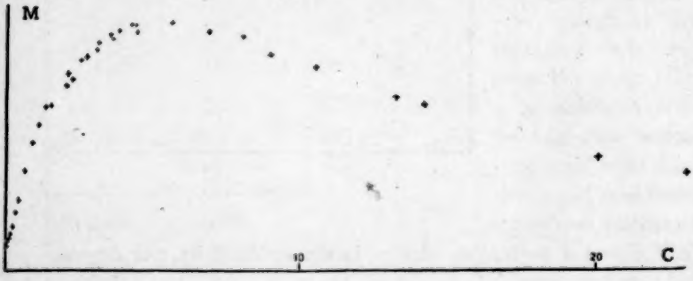

FIGURE 3.

The mass law applied to the dissociation of a binary electrolyte gives the equation $K C_1 = C_2^2$ where C_1 is the concentration of the undissociated substance and C_2 that of one of the ions. It is well known, however, that this equation is not satisfied in the case of all water solutions. Bancroft* has shown that the empirical equation $K C_1 = C_2^n$, where n is a specific constant depending on the nature of the electrolyte, expresses satisfactorily the behavior of any aqueous solution. This quantity n varies from 2 in the case of weak acids and bases down to 1.36 in the case of potassium chloride. If now we could find some still "stronger" electrolyte than potassium chloride, the value of n would doubtless be still smaller. If a substance could be found with a value of n less than 1 the degree of dissociation and consequently the molecular conductivity would increase with the concentration as they do in the case we have been studying.

* Zeit. phys. Chem., **31**, 188 (1899).

From this point of view we see that the increase of molecular conductivity with the concentration, which we have found in the case of potassium iodide in iodine and which others have found in the case of salt solutions in many organic solvents, is a deviation from the mass law in greater degree, but of the same kind and in the same direction, as that which is observed in the case of aqueous solutions of strong electrolytes.

What is the cause of this general deviation from the mass law, and why should it be greater in the case of weak dissociating agents?

Before attempting to answer this question let us give definition to an idea which we shall find useful. If we examine a number of liquids chosen at random, we find that as a rule those liquids which, when pure, are the best conductors of electricity, are, as solvents, the best dissociating agents, and when dissolved in other solvents are themselves the most dissociated. In other words the property of dissociating other substances and the property of being dissociated when pure and when dissolved in other solvents go usually hand in hand. Thus pure nitric acid is a conductor, it dissociates other substances dissolved in it, and is dissociated in other solvents. Benzol has none of these three properties. Let us call a substance possessing these properties to a marked degree an *electrophile*. The best electrophiles are substances which consist of two parts, one having a strong positive, and the other a strong negative electro-affinity, as this term is used by Abegg and Bodländer.* In this category are included most inorganic salts. Ether and the hydrocarbons are types of the poorest electrophiles.

Water occupies an intermediate position. That it stands first or nearly first among known dissociating solvents is due doubtless to the fact that none of the best electrophiles are liquid at ordinary temperatures. The only liquids which are good conductors in a pure state are melted salts.† If these salts could be supercooled to ordinary temperatures their conductivity would still be far greater than that of water, and doubtless their dissociating power too.

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* Zeit. anorg. Chem., **20**, 453 (1899).

† Whether the good conductivity of melted salts is due to a high degree of dissociation or to great mobility of the ions has not hitherto been demonstrated. One of the authors together with Mr. B. S. Lacy has attempted to answer this important question by measuring directly the ionic velocities in melted salts. The experiments, although not yet concluded, have progressed far enough to show that the mobilities of the ions are probably even less than in water. The degree of dissociation must therefore be enormously greater than in the case of any other pure liquids.

Let us see how this idea bears upon the deviations from the mass law, $K C_1 = C_2^2$. Here K is a quantity which does not vary with the concentration in a given medium. In different media however, K has different values, as shown by experiment, and as we should also expect from theory, whether the mass law be derived from the principles of probability or from thermodynamics. If therefore with changing concentration there is an essential change in the character of the medium, K no longer remains a constant but must change as the concentration changes.

In order to give a complete qualitative explanation of the phenomena under consideration we have only to make the assumption that the addition to any solvent of a better or a worse electrophile than itself respectively increases or decreases the electrophilic character of the solvent.

Thus for example, water and acetic acid are both medium good electrophiles. If small quantities of acetic acid are added to water the electrophilic character of the medium is not materially changed and therefore for dilute solutions of acetic acid the mass law holds.

If on the other hand we add to water even a small quantity of a very strong electrophile like potassium chloride the dissociating power of the medium is increased, K increases with the concentration of potassium chloride and we have the familiar deviation from Ostwald's dilution law.

An extraordinarily good confirmation of the view that such deviations are due to a change in the dissociation power of the medium is given by Arrhenius, * who showed that the dissociation of weak acids in water is considerably increased by the addition of small quantities of inorganic salts. In other words a tenth or even hundredth normal salt solution is an appreciably better dissociating solvent than pure water.†

If finally we add to water a substance that is a much poorer electrophile than water itself we should expect a deviation from the dilution law in the opposite direction. That is, the dissociation constant should decrease with the concentration. Such a phenomenon has never been observed, nor, perhaps, is it likely to be until our experimental methods are improved, for to discover this phenomenon it would be necessary to investigate accurately the dissociation of extremely poor electrolytes.

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* Zeit. phys. Chem., 31, 197 (1899).

† It is likewise probable that the dissociation of water itself is considerably increased in strong salt solution. An experimental proof of this would be interesting and important.

However, fully as convincing evidence is offered by the fact demonstrated by Arrhenius * that the dissociation of an electrolyte in water is always diminished by the addition of a non-electrolyte (in other words a very poor electrophile) such as sugar or glycerine.

When now we consider, instead of water, other solvents which are much poorer electrophiles, we should expect results of the same general character, except that the change in dissociating power should be much more pronounced when a strong electrophile is added. So we may explain in these cases deviations from the mass law so great that the degree of dissociation increases with the concentration, as in the case of potassium iodide in iodine.

The Conductivity of Pure Iodine.

Does absolutely pure iodine conduct the current? If so, is this conductivity metallic or electrolytic? If the latter, what are the ions? These are not the least interesting questions raised by our work.

The preparation and study of pure iodine present some difficulties. It seems that iodine acts to some degree upon glass and platinum, and that it therefore absorbs some impurity when it is sublimed and collected upon glass and also when it stands in the cell. For this reason we resublimed some of our best iodine in a simple apparatus made entirely of quartz, and from this transferred it directly to a conductivity cell made of a quartz tube 6–8 mm. in diameter and about 15 cm. long, bent in the form of a U. This was placed in the thermostat, and electrodes of platinum-iridium were introduced just before measuring the conductivity.

The specific conductivity of the iodine obtained in this way was not less than that of the iodine previously used, in fact never less than 3×10^{-5}. Similar results were obtained with iodine twice sublimed in quartz.

We do not feel entirely safe, however, in drawing conclusions from these results until we explain a very perplexing *decrease* in conductivity which was observed when the iodine stood for any length of time in the thermostat. It is hard to account for this unusual behavior. It may be due to some gradual molecular change in the iodine, or to the escape of water or other impurity taken from the air during sublimation, or even to an absorption of impurities while standing, although no case is known where the conductivity of a pure *electrolytic* conductor is lowered by impurities. One experiment was made with iodine sublimed in quartz in a

* Zeit. phys. Chem., **9**, 489 (1892).

vacuum, but this iodine had to be exposed to the air while being introduced into the cell. It gave a conductivity which was of the same order of magnitude as previously observed.

These experiments unfortunately were interrupted before completion. We will therefore postpone a discussion of them until they can be repeated with more care.

It is our intention to return to this subject as soon as circumstances permit, and also to study the solubility and conductivity of other salts in iodine, to determine the molecular weight in these solutions, and finally, if any suitable method can be found for attacking so difficult a problem, to determine from the changes at the electrodes during the flow of the current whether or not the conductivity is altogether electrolytic in character.

Summary.

Potassium iodide is readily soluble in liquid iodine, forming solutions which when concentrated conduct the electric current as well as the best aqueous solutions.

The dependence of the conductivity upon the concentration is determined over a wide range.

In dilute solutions the molecular conductivity increases linearly with the concentration, rising to a maximum and then falling again.

The probable connection is shown between this anomalous behavior and the deviations from Ostwald's dilution law in water solutions. A hypothetical explanation of both these phenomena is offered.

The temperature coefficient of conductivity is negative for dilute solutions, but with increasing concentration passes through zero and becomes positive.

Pure iodine in all probability possesses a conductivity of its own, but this can be definitely determined only by further experiments.